REMOVAL OF HIGH CONCENTRATIONS OF PHOSPHATE FROM AQUEOUS SOLUTION USING ARAGONITE

NADIRA NAJIB1, CHRISTOS CHRISTODOULATOS1, MAHMOUD WAZNE2 and SANTHI JAGUPILLA3

1 Stevens Institute of Technology, Department of Environmental, Civil, and Ocean Engineering
Nadira Najib and Christos Christodoulatos, 2Lebanese American University, School of Engineering, Zakhem Engineering Hall, Mahmoud Wazne, 3TRC Companies, Inc.
nnajib@stevens.edu
Christos.Christodoulatos@stevens.edu

EXTENDED ABSTRACT

High loadings of nutrients such as phosphorus (P) are a major source of eutrophication that is threatening natural water quality worldwide. The excessive concentrations of P present in water bodies originate in agricultural and wastewater effluents, storm water runoff, etc. The disruption of the terrestrial P cycle by anthropogenic activities along with a growing awareness that P is a limited resource call for effective methods to remove and retain P before it reaches natural waters. This study investigates the removal of orthophosphate species (PO$_4^{3-}$-P) by adsorption onto aragonite as a natural adsorbent under a wide range of environmental conditions. Aragonite is a renewable and economical material; it can be used jointly with any best-management practices or as a post-secondary treatment in a wastewater treatment plant to enhance the phosphorus removal and consequently mitigate eutrophication in surface waters. Moreover, the aragonite-adsorbed P product can be used directly as a fertilizer for soils or as a feed material for fertilizer production.

Batch experiments were used in this study to examine the adsorption behavior of PO$_4^{3-}$-P on aragonite as a function of solid-to-liquid ratio, PO$_4^{3-}$-P concentrations, and pH. The results showed that solution pH greatly affects the PO$_4^{3-}$-P removal mechanism. The effect of pH on phosphate removal can be attributed to the nature of P species in solution as well as to hydrolysis reactions on the aragonite surface. Zeta-potential measurements suggested that the uptake is driven by specific adsorption of PO$_4^{3-}$-P onto the aragonite surface. Isotherm studies showed a maximum PO$_4^{3-}$-P removal of the order of 60 mg/g for a solid-to-liquid ratio of 1 g/l. The data are best described by the Langmuir model, which indicates that adsorption of PO$_4^{3-}$-P on aragonite occurs most likely via a monolayer mechanism. A column test permeating an aqueous phosphate solution of 10 g/l through an aragonite-packed bed was studied. The results showed that phosphate breakthrough occurred after approximately 20 pore volumes.
This study showed that aragonite efficiently removes phosphate from aqueous solutions. The electrokinetic results suggest that orthophosphate species are chemically adsorbed onto aragonite over the pH range examined in this study.

Keywords: Phosphate, Adsorbents, Aragonite, Adsorption, Phosphorus, Removal, Eutrophication

1. INTRODUCTION
Nutrient contamination is becoming a major problem facing surface water worldwide. Nutrient contamination comes primarily from municipal wastewater discharge and agricultural runoff, with the latter being the leading source of pollution. Phosphorus has
been demonstrated to be the limiting nutrient in fresh waters (S.R Carpenter et.al, 1998 and Aldridge and Ganf 2003). Excess of phosphorus stimulates the growth of algae, leading to blooms which consume large amounts of dissolved oxygen, suffocating fish and other marine life and creating “dead zones”. The disruption of the terrestrial phosphorus cycle by anthropogenic activities and a growing awareness that phosphorus is a limiting resource, call for effective techniques to remove and retain/recycle/reuse phosphate before it reaches natural waters.

For non-point source pollution, the EPA, in cooperation with its state counterparts, has adopted tools such as best management practices (BMPs) to protect water resources. The most common environmental systems used as BMPs are wetlands and wet ponds. These have shown relatively effective removal rates of P, but have proven to be highly delicate constructs that can frequently and easily be damaged by pollutant overloads (J.N.Carlton et al 2001).

For point-source pollution, there are three main categories of treatment technologies available for phosphorus removal: physical, chemical and biological. In all cases, phosphorus is converted into a solid fraction. This fraction can be an insoluble precipitate salt, a microbial mass in activated sludge, or a plant biomass in constructed wetlands. Of all these methods, adsorption has shown to be the most effective mechanism for phosphate removal. Metal salts have also been shown to be effective for the removal of phosphate compounds. However, metal salts are expensive, and the final product of precipitation is a metal phosphate sludge which is unrecoverable for possible industrial processing (Donnert and Salecker, 1999). Studies have examined the adsorption of phosphates onto calcium carbonate materials such as calcite and monohydrocalcite. K. Karageorgiou et al. have shown that high removal of orthophosphate species removal from aqueous solutions can be achieved by adsorption onto calcite.

The purpose of this research is to investigate the feasibility of phosphate removal using aragonite as a natural adsorbent. Aragonite is a naturally occurring mineral precipitating from ocean water. It is a renewable and economical material that can be used jointly with any BMPs or as a post-secondary treatment in wastewater treatment plants to enhance the removal and recycling of phosphorus as calcium phosphate, and consequently mitigate eutrophication in surface waters. Moreover, the aragonite-adsorbed-phosphate product can be also used as a slow-release soil fertilizer or a feed material for fertilizer production.

2. MATERIALS AND METHODS

2.1. Materials

All chemical reagents used in this study were of A.C.S. grade or better. Synthetic orthophosphate solutions were prepared to conduct adsorption tests. A stock solution of $\text{PO}_4^{3-}\text{-P}$ was prepared by dissolving a set amount of $\text{Na}_2\text{HPO}_4\cdot\text{H}_2\text{O}$ in deionized water. An aliquot of the stock solution was added to a certain volume of deionized (DI) water to prepare the desired phosphate-bearing solutions. Aragonite was obtained from CaCO$_3$ Aragonite Products, Inc. A fixed amount of aragonite was sifted to retain -20 ($d=0.85$ mm) and -200 ($d=0.075$ mm) meshes. The rest was micronized to obtain grain size less than 0.01 mm.

2.2. Batch experiments

All tests, including isotherm tests, were carried out with batch experiments at room temperature. A predetermined amount of aragonite was added to a set volume of a phosphate solution of known concentration in 30 ml polypropylene bottles. The bottles were then sealed and placed in a tumbler for 24 hours. The range of $\text{PO}_4^{3-}\text{-P}$ concentrations was from 20 to 320 mg/l. After mixing, the suspension was filtrated using a Millipore vacuum-operated system using 0.45 μm membrane filters. $\text{PO}_4^{3-}\text{-P}$ concentrations in the filtrate were determined using Hach DR/2010 portable data logging spectrophotometer according to PhosVer3 (Ascorbic Acid) Method.
The values for initial and final $\text{PO}_4^{3-}$ concentrations were used to calculate the $P$ removal capacity (mg/g) as the amount of $P$ removed at equilibrium per volume of sample as follow:

$$q = \frac{(C_0 - C_e) \times V}{m}$$

Where; $q =$ uptake of $\text{PO}_4^{3-}$ (mg/g), $C_0 =$ initial $P$ concentration of the solution (mg/l), $V =$ volume of solution (L), and $m =$ mass of sorbent (g).

### 2.3. Column experiments:

A column test was performed to evaluate the phosphate removal capacity by aragonite in a continuous system at room temperature. The Kontes Flexcolumn column (Thermo Fisher Scientific Inc., Waltham, MA) used in this experiment was 18 cm long and had an inner diameter of 1.8 cm. The column was permeated with a phosphate solution up to 100 pore volumes (PVs). The aragonite sample was washed with DI water, and then packed moist into the column to avoid the formation of air bubbles. The dry weight of aragonite packed into the column was 54.68 g, which yielded a porosity of 0.6 (specific gravity = 2.95). A piece of 20 µm filter paper was placed at each end of the packed aragonite media to prevent migration of fine aragonite particles through the column. Tubing made of inert Tygon (Nalgene, Rochester, NY) was used for all external piping networks. The leaching process was conducted in a continuous upflow mode to promote saturated flow conditions and to mitigate short-circuiting of flow. An average flow rate of 0.1 L/hr was chosen for this study, which yielded an average column retention time of approximately 16 minutes. The initial concentration of phosphate ($\text{PO}_4^{3-}$) was 10 mg/L. The influent solution was mixed continuously using a magnetic stirrer. A Master-Flex peristaltic pump was used to introduce the aqueous phosphate solution into the column. The effluent solution was sampled at pre-set time intervals, and the total volumes of the permeated solutions were recorded.

### 2.4. Zeta potential

Zeta-potential measurements were carried out using 1 g/L of micronized aragonite suspensions in the presence and absence of 100 mg/L $\text{PO}_4^{3-}$ solution. The suspensions were prepared in 30 mL bottles and placed on a rotator for 24h at 25°C. After mixing, the equilibrium pH of the samples was measured, and the aliquots were filtered through 11 µm filter paper (Whatman No 1), then they were dispersed by a thermostated shaker bath for 15 minutes. One mL of each filtrate was introduced into a polystyrene cuvette and Zeta potential was measured using a Zetasizer Nano series® instrument (Malvern, Worcestershire, UK) using dynamic light scattering (DLS). The Helmholtz–Smoluchowski equation was applied to convert measured electrophoretic mobilities to ζ–potential. All samples were prepared in duplicates. The filter pore size was selected based on the Malvern Zetasizer particle-size range limitation for Zeta potential measurement between 5 nm and 10 µm.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Solid-to-liquid Ratio and Grain Size on P Removal

The removal capacity of aragonite, with different grain sizes, was determined by batch experiments. Two solid-to-liquid ratios, 10 g/L and 1 g/L, were used, with an initial $\text{PO}_4^{3-}$ concentration of 100 ppm. The results are given in Figures 1 and 2. It is observed that increasing the solid-to-liquid ratio from 1 g to 10 g per 1 liter solution for different grain sizes increased the removal percentage of $P$ for all different grain sizes. Decreasing the grain size from 0.85 mm to 0.075 and 0.01 mm significantly increased the P removal capacity. However, there was no difference on the P removal capacity between 0.075 and 0.01 grain sizes.
3.2. **Effect of pH on the Adsorption Mechanism of Phosphate**

The effect of pH on the removal of phosphates with micronized aragonite was investigated at room temperature. The initial pH of the experiment was pre-adjusted to different values between 5 and 13 with 1 M NaOH solution. The tests were carried out with an initial PO$_4^{3-}$-P concentration of 100 ppm and a solid-to-liquid ratio of 1 g/L. From Figure 3, it seems that the adsorption process of phosphate onto aragonite is pH dependent. At initial pH range between 5 and 7 (the final pH from 7.6 to 8.2), P removal was between 59 and 77 mg/g. However, as the initial pH increased from 7 to 12 (the final pH 8.2 to 11.6), the P removal decreased. The removal efficiency then increased with the increase of pH from 12 to 13 (final 11.6 to 12.4). From Figure 4, it can be observed that when 100 ppm PO$_4^{3-}$-P is added to aragonite suspensions, the charge on the surface of aragonite drops in the pH range between 6 and 12. The electrokinetic results suggest that orthophosphate species are chemically adsorbed onto aragonite for the pH range examined in this study. The effect of pH on P removal can be attributed to the nature of phosphate species in the solution as well as the hydrolysis reactions on aragonite surface as shown in Figure 3.

In water, the reactions of phosphate species are as follows (Snoeyink and Jenkins, 1983):

\[
\begin{align*}
\text{PO}_4^{3-} + \text{H}_2\text{O} & = \text{HPO}_4^{2-} + \text{OH}^-; \quad \text{pK}_1 = 1.68 \\
\text{HPO}_4^{2-} + \text{H}_2\text{O} & = \text{H}_2\text{PO}_4^- + \text{OH}^-; \quad \text{pK}_2 = 6.79 \\
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} & = \text{H}_3\text{PO}_4 + \text{OH}^-; \quad \text{pK}_3 = 11.67 \\
\text{H}_2\text{O} & = \text{H}^+ + \text{OH}^-; \quad \text{pK}_w = 14
\end{align*}
\]
The hydrolysis reactions for the cationic and anionic species on aragonite surface are described by the following reactions (Karageorgiou et al and Liu et al.):

\[ \text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}, \ pK_S = 3.25 \]
\[ \text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-, \ pK = 3.67 \]
\[ \text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+, \ pK = -0.82 \]
\[ \text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+, \ pK = -1.4 \]

From the speciation diagram for phosphate (Figure 4), in the pH region from 7.6 to 8.2, phosphorus species are mainly in the form of H\(_2\)PO\(_4^-\). At pH between 8.2 and 11.6, HPO\(_4^{2-}\) species predominate over PO\(_4^{3-}\), while at pH higher than 11.6, PO\(_4^{3-}\) is the main P species. Based on the aforementioned reactions, the removal process could be described through the following reactions:

\[ \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- = \text{CaH}_2\text{PO}_4^+, \ pK = -1.08 \]
\[ \text{Ca}^{2+} + \text{HPO}_4^{2-} = \text{CaHPO}_4, \ pK = -7.0 \]
\[ \text{Ca}^{2+} + \text{PO}_4^{3-} = \text{CaPO}_4, \ pK = -6.5 \]
\[ 3\text{Ca}^{2+} + 2\text{PO}_4^{3-} = \text{Ca}_3(\text{PO}_4)_2, \ pK = -26 \]
\[ 3\text{Ca}^{2+} + \text{HPO}_4^{2-} + \text{HCO}_3^- = \text{Ca}_2\text{HPO}_4\text{CO}_3 + \text{H}^+, \ pK = 1.33 \]
\[ \text{Ca}_2\text{HPO}_4\text{CO}_3 = \text{Ca}_2\text{PO}_4\text{CO}_3 + \text{H}^+, \ pK = 8.3 \]
\[ 10\text{CaCO}_3 + 2\text{H}^+ + 6\text{HPO}_4^{2-} + 2\text{H}_2\text{O} = \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 10\text{HCO}_3^-, \ pK = -32 \]

**Figure 3**: Effect of pH on PO\(_4^{3-}\)- P adsorption onto aragonite

**Figure 4**: Distribution diagram for phosphate as a function of pH
3.3. Isotherm Results:

An adsorption isotherm was constructed for the phosphate removal by aragonite. The PO$_4^{3-}$-P removal versus equilibrium PO$_4^{3-}$-P concentrations in solution was plotted as shown in Figure 4.

Freundlich and Langmuir models were attempted to describe the equilibrium uptake data.

The Langmuir model assumes a uniform adsorption energy among adsorption sites on a homogenous surface. The Langmuir model (Langmuir 1918) is given by equation (1):

$$ q_e = q_{\text{max}} \frac{K_L C_e}{1 + K_L C_e} $$

where $q_e$ (mg/g) is the Langmuir monolayer sorption capacity and $C_e$ (mg/L) is the equilibrium concentration of PO$_4^{3-}$-P in the solid and liquid phase, respectively. $q_{\text{max}}$ (mg/g) is the Langmuir monolayer sorption capacity $K_L$ is the Langmuir coefficient relating to adsorption intensity (l/mg).

The Freundlich isotherm is an empirical relationship employed to describe heterogeneous systems. This isotherm does not predict any saturation; thus, infinite surface coverage is predicted mathematically, indicating a multilayer adsorption on the surface of the adsorbent.

The Freundlich model (Freundlich 1926) is described by the following equation (2):

$$ q_e = K_F C_e^{1/n} $$
Where; \( K_F \) [mg/g(L/mg)]\(^{1/n}\) is the relative sorption capacity and \( 1/n \) is the intensity of sorption. Non-linear regression procedures were used to estimate the parameters for the two adsorption isotherm models in the removal of PO\(_4^{3-}\)-P. Table 1 summarizes the estimated parameters for both Langmuir and Freundlich models. Based on the higher values of correlation coefficients (\( R^2 \)) for the Langmuir model compared to the Freundlich model, the adsorption data are better described by the Langmuir model. This indicates that the adsorption mechanism of PO\(_4^{3-}\)-P is most likely a monolayer adsorption mechanism onto the surface of aragonite.

**Table 1: Isotherm parameters for adsorption of PO\(_4^{3-}\)-P**

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th></th>
<th>Freundlich</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>75.67</td>
<td>0.03</td>
<td>8.95</td>
<td>0.38</td>
</tr>
<tr>
<td>( K_L ) (mg/l)</td>
<td>0.9863</td>
<td>42.66</td>
<td>0.8825</td>
<td>365.37</td>
</tr>
</tbody>
</table>

### 3.4. Electrokinetic Results

The effect of addition of P and the effect of pH on the surface charge of aragonite were investigated using aragonite suspensions in the presence and absence of 100 mg/L of PO\(_4^{3-}\)-P. The results are presented in Figure 5. The Zeta-potential values for aragonite suspensions in the absence of P were greater than those in the presence of P over a pH range from 6.5 to 10.5. The electrokinetic results show that the addition of P into the aragonite suspensions resulted in a decrease in the surface charge of aragonite. The electrokinetic results suggest that P species are chemically adsorbed onto aragonite for the pH range examined in this study.

### 3.5. Column Test Result

The results for the phosphate column are summarized in Table 2. Figure 1 presents the effluent P concentrations from the aragonite column at different pore volumes. The test results show that P breakthrough occurred after approximately 20 pore volumes. However, complete breakthrough (C/Co = 1) was not achieved during the test duration of 100 pore volumes.

**Table 2. PO\(_4^{3-}\)-Column Leaching Results**

<table>
<thead>
<tr>
<th>Pore Volumes</th>
<th>PO(_4^{3-}) (mg/l)</th>
<th>Pore Volumes</th>
<th>PO(_4^{3-}) (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.184</td>
<td>14</td>
<td>0.031</td>
</tr>
<tr>
<td>1</td>
<td>0.184</td>
<td>15</td>
<td>0.031</td>
</tr>
<tr>
<td>2</td>
<td>0.153</td>
<td>16</td>
<td>0.092</td>
</tr>
<tr>
<td>3</td>
<td>0.153</td>
<td>17</td>
<td>0.153</td>
</tr>
<tr>
<td>4</td>
<td>0.13</td>
<td>18</td>
<td>0.276</td>
</tr>
<tr>
<td>5</td>
<td>0.13</td>
<td>19</td>
<td>0.582</td>
</tr>
<tr>
<td>6</td>
<td>0.092</td>
<td>20</td>
<td>1.027</td>
</tr>
<tr>
<td>7</td>
<td>0.061</td>
<td>23</td>
<td>3.202</td>
</tr>
<tr>
<td>8</td>
<td>0.061</td>
<td>26</td>
<td>4.643</td>
</tr>
<tr>
<td>9</td>
<td>0.061</td>
<td>29</td>
<td>5.654</td>
</tr>
<tr>
<td>10</td>
<td>0.061</td>
<td>32</td>
<td>6.451</td>
</tr>
<tr>
<td>11</td>
<td>0.031</td>
<td>35</td>
<td>6.972</td>
</tr>
<tr>
<td>12</td>
<td>0.031</td>
<td>82</td>
<td>9.515</td>
</tr>
<tr>
<td>13</td>
<td>0.031</td>
<td>96</td>
<td>9.684</td>
</tr>
</tbody>
</table>
4. CONCLUSION

The sorption behavior of phosphate onto aragonite as a natural adsorbent was examined as a function of solid-to-liquid ratio, phosphate loadings, and pH. Aragonite with a grain size less than 0.075 mm showed a removal capacity greater than 75% with a solid-volume ratio of 1 g/l. This study showed that phosphate removal depends on the solution pH. The effect of pH on phosphate removal can be attributed to the nature of phosphorus species in the solution, as well as to hydrolysis reactions on the aragonite surface. The electrokinetic results suggest that orthophosphate species are chemically adsorbed onto aragonite over the pH range examined in this study. Finally, the column study indicated that phosphate breakthrough occurred after approximately 20 pore volumes.

REFERENCES